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ORIGINAL ARTICLE

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The effect of ceramic coating of fire-retardant wood on combustibility and weatherability

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Abstract In order to develop a fireproof wooden material, the synergic effect of fire-retardant chemicals and wood coatings was studied. The fire performance was evaluated by cone calorimeter. Impregnation of fire retardants including polyphosphatic carbamate, and ceramic coatings including alkoxy metal salt improved the fire performance of wooden materials. This treatment made it possible to meet the guidelines for fire performance of noncombustible materials in Japan. In addition to the vacuum–pressure impregnation treatment, hot-and-cold-bath impregnation treatment is an effective way to develop fire-retardant wood by impregnating fire retardant and ceramic coating. The weatherability of the developed material was also investigated. The ceramic coating was resistant to light and moisture.

Key words Fire-retardant wood · Polyphosphatic carbamate · Ceramic coating · Cone calorimeter test · Weatherability of coating

Introduction

Fire performance materials in Japan are classified into three categories: noncombustible material, quasi-noncombustible material, and fire-retardant material. Since the Building Standards Law was revised to permit wooden noncombustible materials, quite a few wooden noncombustible and quasi-non-combustible materials have been developed.

Vacuum–pressure impregnation is very popular for developing fireproof wooden materials. Boron/borate and inorganic phosphate/nitrogen are often used for fire-retardant chemicals. Harada et al.[1] reported that a 15-mm-thick wood specimen impregnated with more than 80 kg/m^3 of fire retardant (polyphosphatic carbamate) showed the performance of a fire-retardant material and a specimen with more than 160 kg/m^3 of chemicals met the criteria for quasi-non-combustible materials.

However, there are also many complaints about problems such as efflorescence, in which impregnated chemicals are drawn out as white crystals by moisture absorption. Painting is one solution, and surface coating is also important for finishing. However, if the coating material is flammable, the paint may enhance the combustibility of the products. Moreover, coating characteristics can also affect the durability of fire-retardant-impregnated wood. Östman et al.[2] and Winandy[3] reviewed the durability of fire-retardant-treated wood under humid conditions. However, the synergistic effect of fire-retardant chemicals and coating for the fire performance of wood material has not been studied.

In this study, we examined whether the ceramic coating promotes the fire performance of fire-retardant-impregnated wood. The coating characteristics that inhibit the fire-retarding properties of wood were also studied.

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Experimental

Fire test

Test specimens

Fire-retardant solutions with different concentrations were impregnated into wood to determine the best treatment conditions for preparing fire-retardant-treated wood. Half of the fire-retardant-treated wood was painted with a ce-

ramic coating to investigate the effectiveness of ceramic coating. The specimens were 20-mm-thick Japanese red pine (*Pinus densiflora* Siebold et Zuccarini) and Japanese linden (*Tilia japonica* Simonkai). Six boards with dimensions of 4000 (L) × 120 (T) × 20 mm (R) were prepared for each species and three boards of 300 (L) × 120 (T) × 20 mm (R) were obtained from one piece of lumber.

The intumescent fire-retardant chemical was commercially available Non-nen W2-50 (Marubishi). The concentration of the undiluted solution was 50%, and the pH ranged between 5.4 and 6.8. The main component of the fire retardant is polyphosphatic carbamate, and the degree of polymerization n is 5–10. The chemical compound is as follows.

$$NH_2CO\text{-}[OPO(OA)]_n\text{-}OCNH_2, \quad \text{where } A{=}H, NH_4, CONH_2$$

The fire retardant was diluted with water to prepare 6.25%, 12.5%, 25%, and 37.5% solutions. Water was also used as a control solution (0% fire-retardant). These solutions were impregnated using a pressure and pressure-reducing chemical feeder (Yasujima). The processing procedure was as follows. The specimens were decompressed at 25 torr (3333 Pa) for 2 h, pressured with air [9.8 kg/cm^2 (0.96 MPa)] for 24 h, and then left at atmospheric pressure for 24 h. After impregnation, the specimens were dried under atmospheric conditions (15°–20°C) for 1 week, then at 45°C for 2 weeks. After being dried, the impregnated wood specimens were planed to 15 mm in thickness. The amount of fire-retardant chemicals was calculated using Eq. 1.

$$AC = \{[W_1/(U_1/100 + 1)] - [W_0/(U_0/100 + 1)]\}/V_0 \qquad (1)$$

where AC is the concentration of the active constituent of fire-retardant chemicals (kg/m^3); W_0 is the specimen mass before treatment (kg); U_0 is the moisture content of the wood specimen before treatment (%); W_1 is the specimen mass after treatment (kg); U_1 is the moisture content of the wood specimen after treatment (%); and V_0 is the specimen volume before treatment (m^3).

Figure 1 shows the relationships between concentration of fire-retardant solution and impregnated active constituent of fire-retardant chemicals. When the concentration of the solution was high, the amount of chemicals in the Japanese linden was more than that in Japanese red pine. The 30-cm-long wood specimens were cut into two. The ceramic paint (CRB-90, Nippan Kenkyujo) was coated on the surface of one half of the cut specimens. The surface of these specimens was painted four times, and the back face was painted three times. The other half of the specimens were not painted. CRB-90 (CRB) is an antibacterial, mildew-proof, high-strength, and corrosion-resistant paint with major components of SiO_2 and Ag. After being dried, the specimens were cut to prepare cone calorimeter test specimens. The dimensions were 100 × 100 mm.

The experiment above was conducted to investigate the synergistic effects of fire retardants (polyphosphatic carbamate) and ceramic coating. However, a simpler method is preferable. Next, the hot-and-cold-bath impregnation treatment (HCBIT) was studied. Fire-retardant solution was impregnated into three 6-mm-thick Japanese linden specimens by the HCBIT. These three treated wood specimens were laminated, and then each specimen was planed to a thickness of 15 mm before coating with ceramic paint. Twenty-one Japanese linden specimens of 2000 (L) × 140 (T) × 6 mm (R) were prepared and impregnated with a 30% fire-retardant solution (Non-nen W2-50) by the HCBIT.

The treatment procedure was as follows; boiling for 2 h, bathing in cold solution for 48 h, conditioning at room temperature for 3 h, and then drying at 80°C for 3 days. The amount of active ingredients ranged from 181 to 272 kg/m^3 (average: 229 kg/m^3). Seven pieces of three-ply laminated lumber with average chemical impregnation of 230 kg/m^3 were cut from these treated Japanese linden specimens. An aqueous polymer isocyanate adhesive (PI6000, Oshika) was used for laminate bonding. Specimens were pressed at 10 kgf/cm^2 (0.98 MPa) for 3 h. After adhesive bonding, they were cut and planed to dimensions of 2000 (L) × 130 (T) × 15 mm (R). Some of these specimens were further cut into pieces measuring 330 (L) × 130 (T) × 15 mm (R) and were coated with the following coatings:

1. CRB-90 (CRB) (Nippan Kenkyujo) with main components of SiO_2 and Ag and coverage of 50 g/m^2
2. AQUREX No. 3400 (AR) (Washin) waterborne urethane coatings with coverage of 50 g/m^2
3. Osmo color clear (OS) (Osmo) with coverage of 30 g/m^2
4. Kihada-toryo (UP) solvent-borne polyurethane coatings (Saito) with coverage of 50 g/m^2

After coating, they were dried and cut into pieces measuring 100 (L) × 100 (T) × 15 mm (R) for the cone calorimeter test. At the same time, specimens with concentrations of impregnated fire-retardant chemicals of 0, 80, 113, 170, 141, 205, and 216 kg/m^3 were also coated with CRB.

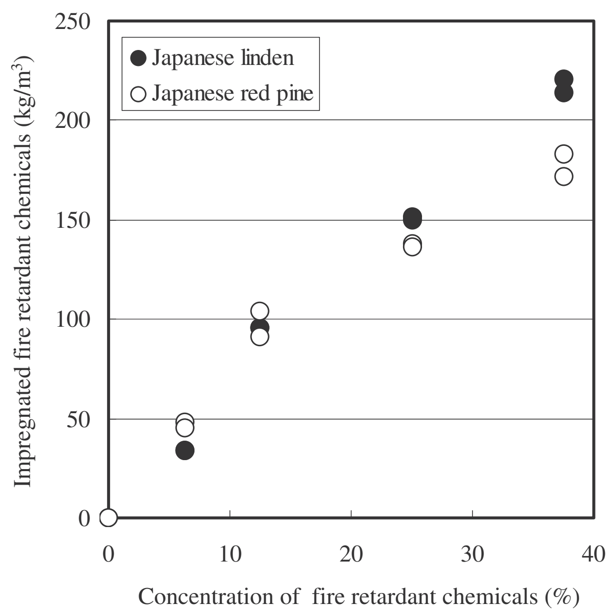

Fig. 1. Concentration of active constituent of fire-retardant chemicals in Japanese linden and Japanese red pine plotted against the concentration of the impregnation solution. Results are shown for impregnation with Non-nen W2-50 (Marubishi) solutions with active ingredient concentrations of 6.25%, 12.5%, 25.0%, and 37.5%

Cone calorimeter test

In Japan, the Building Standards Law stipulates that noncombustible material, quasi-non-combustible material, and fire-retardant material must have 20-min, 10-min, and 5-min noncombustibility, respectively. The fire performance is evaluated by the cone calorimeter test (ISO 5660-1).[4] The test is conducted at 50 kW/m^2 heat flux, and the criteria are as follows:

1. The total heat release in the heating time is 8 MJ/m^2 or less.
2. No cracks or holes penetrating the back surface during the heating time.
3. The heat release rate that exceeds 200 kW/m^2 does not last more than 10 s during the heating time.

In addition to this test, a gas toxicity test using mice is also required.

In this study, we evaluated the fire performance of the specimen using a cone calorimeter (Atras, cone 2a). The specimens were placed horizontally under a cone heater with a heat flux of 50 kW/m^2. The heating time was 10 or 20 min. A stainless steel cover with an opening of 0.0088 m^2 on the upper part was attached to the specimen in order to minimize the effect of heating on the side and to prevent warping of the specimens. The data were recorded in a computer every 2 s. The time to ignition (t_{ig}), the heat release rate (HRR), the total heat release for 5, 10, and 20 min (THR_5, THR_{10}, THR_{20}), and the appearance of the specimen after the test were evaluated.

Performance testing for coatings

The performance of coatings of three-ply Japanese linden boards containing 230 kg/m^3 of impregnated fire-retardant chemicals was tested. The main purpose was to evaluate the performance of CRB. However the performance of AR, OS, and UP was also tested for comparison. Coatings were brushed three times, and the specimens were dried for 24 h in an ambient atmosphere. The dimensions of the specimens were 150 (L) × 70 (T) × 15 mm (R).

The resistance to humidity was evaluated according to JIS K 5600-7-2[5] (continuous condensation) using a differential temperature cabinet (Suga) at 50°C and 95% relative humidity. The accelerated weathering was conducted according to JIS K 5600-7-7[6] (exposure to filtered xenon-arc radiation) using a xenon long-life weather meter (Suga) under the condition of no rainfall. The color difference was measured every 24 h.

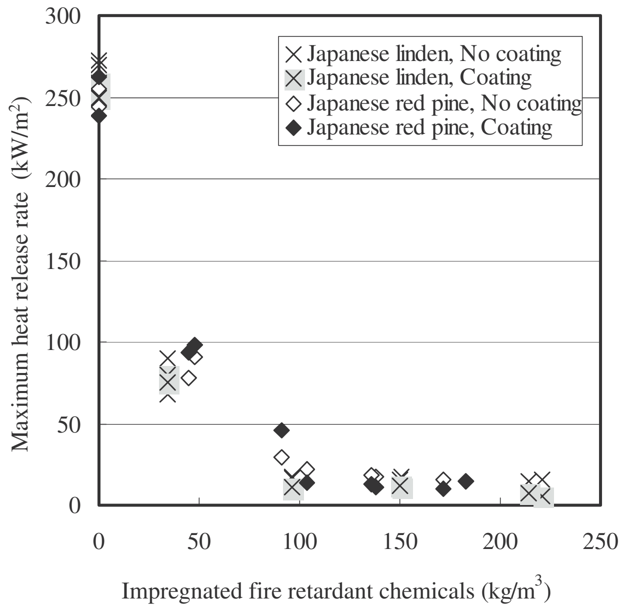

Fig. 2. Effect of CRB-90 ceramic paint (CRB) coating on maximum heat release rate of fire-retardant-impregnated wood compared with uncoated control samples. Cone calorimeter tests were conducted at 50 kW/m^2 heat flux

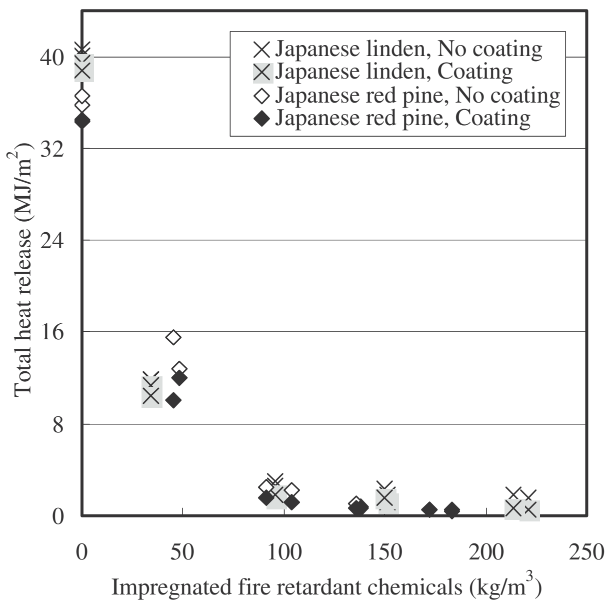

Fig. 3. The effect of CRB coating on total heat release for 5 min of the fire-retardant-impregnated wood compared with uncoated control samples. Cone calorimeter tests were conducted at 50 kW/m^2 heat flux. Total heat release of fire-retardant material is required to be 8 MJ/m^2 or less for 5 min

Results and discussion

Effects of fire-retardant chemicals and coatings

The effects of wood species, the amount of fire retardant, and coatings were compared. Figure 2 indicates the maximum heat release rate (HRR_{max}). Figures 3, 4, and 5 show THR_5, THR_{10}, and THR_{20}, respectively.

It is clear that increasing the amount of fire-retardant chemicals reduced the maximum HRR and THR regardless of wood species. The THR of the CRB-coated specimens was a little smaller than that of the specimens without coating. We can say that the CRB coating is slightly effective for developing fire-retardant wooden materials.

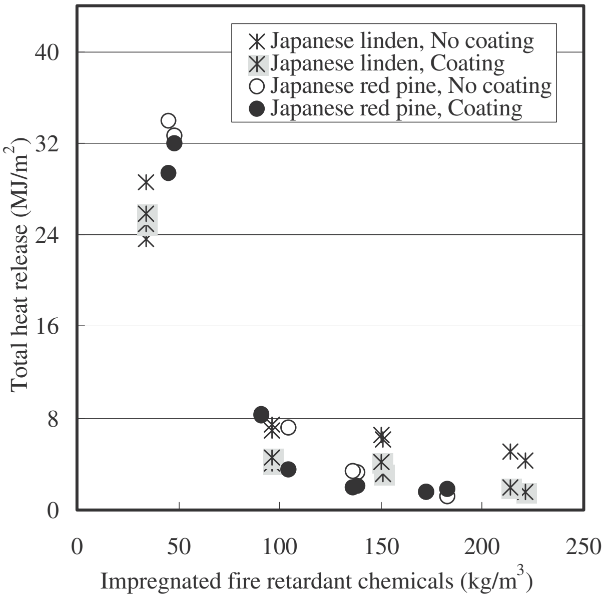

Fig. 4. The effect of CRB coating on total heat release for 10 min of the fire-retardant-impregnated wood compared with uncoated control samples. Cone calorimeter tests were conducted at $50\,kW/m^2$ heat flux. Total heat release of quasi-non-combustible material is required to be $8\,MJ/m^2$ or less for 10 min

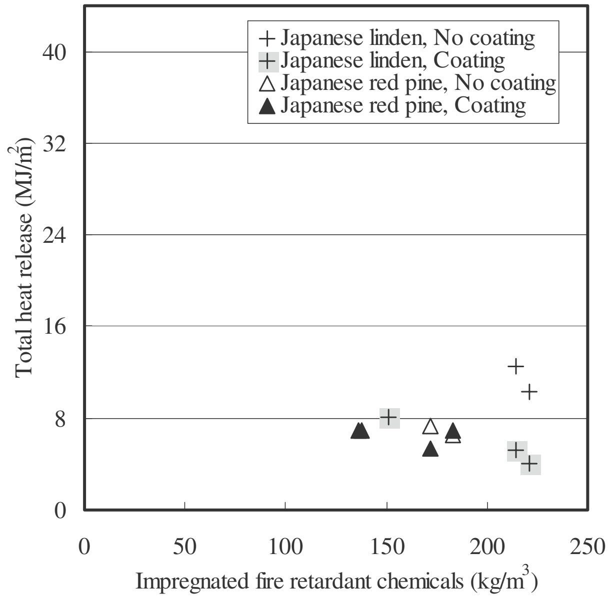

Fig. 5. The effect of CRB coating on total heat release for 20 min of the fire-retardant-impregnated wood compared with uncoated control samples. Cone calorimeter tests were conducted at $50\,kW/m^2$ heat flux. Total heat release of noncombustible material is required to be $8\,MJ/m^2$ or less for 20 min

Regarding the difference between wood species, the following tendency was observed. When the fire-retardant chemical was not impregnated and the CRB coating was not brushed, the average values of HRR for 180 s and 300 s after ignition of Japanese linden (density: $380\,kg/m^3$) were 145 and $140\,kW/m^2$, respectively, whereas those of Japanese red pine (density: $530\,kg/m^3$) were 131 and $128\,kW/m^2$. The average HRR of Japanese linden was slightly larger than that of Japanese red pine despite its lower density.

Roughly speaking, the average HRR of wood correlates with the density; however, the correlation coefficient is not good. According to Harada,[7,8] the average HRR of wood is affected by density, chemical components, and tissue structure. When a small amount of fire-retardant chemicals was impregnated and CBR was not brushed, the THR of Japanese red pine was slightly higher than that of Japanese linden. On the other hand, when a sufficient amount of chemicals was impregnated, the THR of Japanese red pine was less than that of Japanese linden. This may depend on the wood species, but it will take further study to identify the mechanism.

The CRB coating was rather effective for Japanese linden, but not for Japanese red pine. Figure 6 shows the total heat release curves and indicates that the CBR coating had a positive effect on the treated Japanese linden. According to Fig. 4, the total heat release for 10 min of Japanese red pine and Japanese linden could be kept to less than $8\,MJ/m^2$ by impregnating $100\,kg/m^3$ fire-retardant chemicals and coating with CRB to make them quasi-non-combustible materials. In addition, Japanese red pine impregnated with $150\,kg/m^3$ fire retardant and Japanese linden impregnated with $210\,kg/m^3$ fire retardant could be made into noncombustible materials by coating them with CRB (Fig. 5).

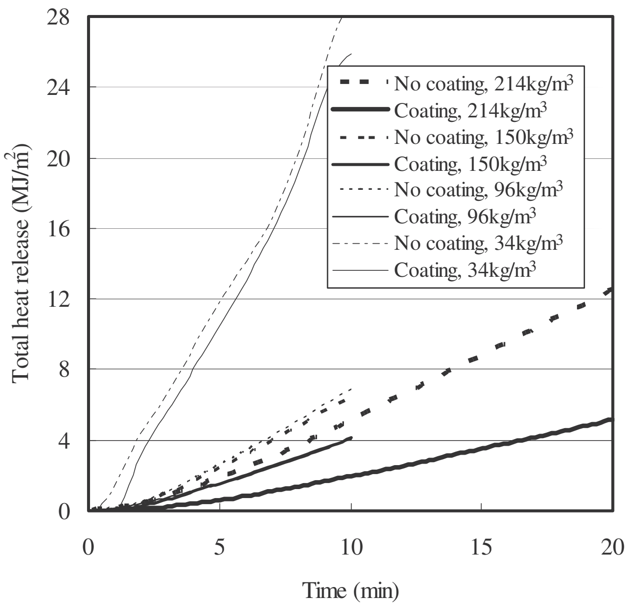

Fig. 6. Total heat release rate curves of treated Japanese linden specimens impregnated with different concentrations of fire retardant. Results for coated and uncoated specimens are shown for each fire retardant concentration. Cone calorimeter tests were conducted at $50\,kW/m^2$ heat flux

The CRB is made up of a coating containing hydrolysis and condensation polymers, and contains alkoxy metal salt that together make a hydrophobic and shielding glass film on the wood surface. The synergistic effect of the alkoxy metal salt and fire-retardant-containing phosphate promotes the fire-retardant character, and a lesser amount of fire retardant can still satisfy the fire performance of a non-

combustible material. When a wood specimen was heated, it pyrolyzed and the combustible mixture gas ignited and burned continuously. Phosphate-containing fire retardant has an effect of reducing the amount of combustible gas. Coating with the alkoxy metal salt enhanced the performance of the fire retardant and reduced the HRR from the fire-retardant-treated wood specimen by keeping out heat, delaying the generation of combustible gas, and sealing it in the wood.

Hot-and-cold-bath impregnation treatment and coatings

As mentioned above, it is clear that the combination of fire-retardant impregnation and coatings containing alkoxy metal salt enhanced the fire-retardant character. In the manufacturing of products, a simple approach is preferable. In this study, the HCBIT was examined. It consists of two processes, the hot bath treatment in which the wood specimens are immersed in boiling water, and the cold bath process in which the boiled specimens are immersed in a cold fire-retardant solution. These processes simplify the impregnation process because there is no pressure treatment.

However the HCBIT has little advantage in impregnation ratio compared with the vacuum and pressure impregnation treatment (VPIT), and makes it difficult to impregnate fire retardant into thick wood specimens. Therefore, we treated 6-mm-thick Japanese linden wood specimens and made three-ply laminated wood. The surface was coated with CRB. When fire-retardant-treated wooden materials are used for interior finishing, a coating is necessary to provide a finish and to prevent crystals of fire retardant from precipitating on the surface. In addition to CRB, the fire performance of other common wood coatings was studied.

The cone calorimeter test results for the three-ply Japanese linden specimens with the HCBIT and coating are listed in Table 1. Even if the concentration of fire-retardant solution is the same, the amount of chemicals impregnated by HCBIT was smaller than that impregnated by VPIT. The THR_{10} of the specimen with 113 kg/m^3 of impregnated fire retardant and coated with CRB was 12.2 MJ/m^2. According to these results, 150 kg/m^3 of fire-retardant chemicals was needed to keep THR_{10} at less than 8 MJ/m^2.

Table 1 shows the THR values for three-ply Japanese linden specimens impregnated with the four types of coatings at fire retardant concentrations of 230 kg/m^3 or more. The average THR_{10} values of specimens coated with CRB, AR, OS, and UP were 2.7, 7.9, 6.1, and 7.1 MJ/m^2, respectively, in nominated fire retardant concentration range. The THR of CRB-coated specimens was lower than those of the other coated specimens. All but one of the CRB coated specimens did not ignite and their HRR_{max} was 8–9 kW/m^2. However, the AR-coated specimens ignited at 20–31 s and the HRR_{max} was 38–116 kW/m^2, the OS-coated specimens ignited at 12–15 s (one specimen did not ignite) and the HRR_{max} was 23–74 kW/m^2, and the UP-coated specimens ignited at 13–19 s and the HRR_{max} was 111–124 kW/m^2.

Table 1. Cone calorimeter test results of treated three-ply Japanese linden boards

Coatings	Fire-retardant chemicals[a] (kg/m^3)	t_{ig} (s)	HRR_{max} (kW/m^2)	THR_{10} (MJ/m^2)	Criteria
CRB	0	16	217	77.0	–
CRB	80	10	151	35.7	–
CRB	113	14	80	12.2	FR
CRB	170	272	42	6.6	QN
CRB	141	385	16	4.1	QN
CRB	205	410	29	5.9	QN
CRB	216	498	26	4.1	QN
CRB	234	473	9	2.8	QN
CRB	238	NI	9	2.6	QN
CRB	236	NI	8	2.7	QN
AR	234	31	38	7.5	QN
AR	238	29	57	8.0	QN
AR	236	21	116	8.4	FR
OS	234	NI	22	5.4	QN
OS	238	12	63	6.3	QN
OS	236	15	74	6.5	QN
UP	234	13	121	6.9	QN
UP	238	19	111	6.6	QN
UP	236	18	124	7.7	QN

Cone calorimeter tests were conducted at 50 kW/m^2 heat flux
CRB, CRB-90; AR, AQUREX No.3400; OS, Osmo color clear; UP, Kihada-toryo; t_{ig}, time to ignition; HRR_{max}, maximum heat release rate; THR_{10}, total heat release for 10 min; NI, no ignition; FR, fire-retardant material; QN, quasi-non-combustible material
[a] Amount of fire-retardant chemicals impregnated by hot-and-cold-bath impregnation treatment

Accordingly, CRB was the most effective of the four coatings for the fire-retardant-impregnated Japanese linden. This indicates that the CRB coating can be used to develop quasi-non-combustible or noncombustible materials that require relatively small amounts of fire retardant.

Performance of coatings

In addition to the fire performance, resistance to discoloring and changes in temperature and humidity is necessary for the fire-retardant-treated wood. In the case of wood that is impregnated with water-soluble fire retardant, the fire retardant absorbs moisture and the crystal often comes to the surface in a powdery state. Coating should help to prevent this. However, the coatings should also have high light stability and moisture resistance.

The results of the accelerated weathering test for coated wood specimens (three-ply fire-retardant-treated Japanese linden boards) are shown in Fig. 7. The ΔE^* of AR- and OS-coated wood was 6–8 for 24 h and 18–23 for 120 h, and it was found that AR and OS were more susceptible to light. On the other hand, the ΔE^* of UP- and CRB-coated wood was 10–12 for 120 h, and they showed good light stability.

Figure 8 shows the test results of the resistance to humidity. The fire-retardant chemicals came to the surface at 48 h for AR coating and at 144 h for OS coating. On the other hand, UP and CRB prevented the fire-retardant chemicals from separating out for 240 h. The CRB forms a vitreous film and the UP forms three-dimensional chemical bonds.

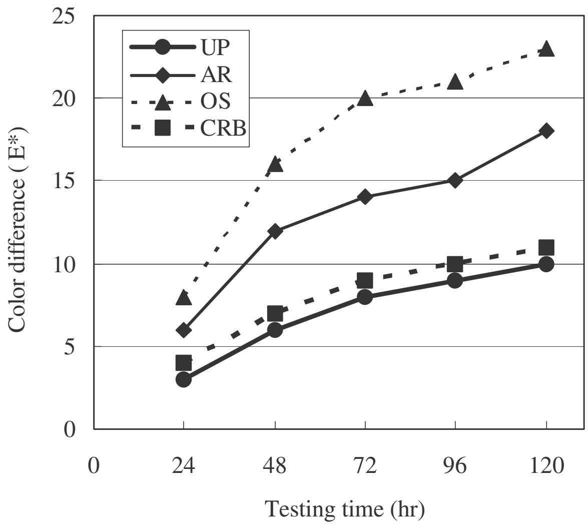

Fig. 7. Color difference in the accelerated weathering test. Accelerated weathering was conducted according to JIS K 5600-7-7 (exposure to filtered xenon-arc radiation). *CRB*, fire-retardant-treated Japanese linden coated with CRB-90; *AR*, fire-retardant-treatment Japanese linden coated with AQUREX No. 3400; *OS*, fire-retardant-treated Japanese linden coated with Osmo color clear; *UP*, fire-retardant-treated Japanese linden coated with Kihada-toryo

These strengthen the coating and provide moisture resistance for fire-retardant-impregnated wood in humid conditions. These coatings could be used under normal room conditions without problems.

Conclusions

In the vacuum–pressure impregnation treatment, $100\,kg/m^3$ of fire-retardant chemicals and $50\,g/m^2$ of ceramic coating gave wood specimens quasi-non-combustible fire performance in which the total heat release for 10 min was less than $8\,MJ/m^2$. By coating with CRB, Japanese red pine impregnated with $150\,kg/m^3$ of fire retardant and Japanese linden impregnated with $210\,kg/m^3$ of fire retardant showed the fire performance of noncombustible material. In the hot-and-cold-bath impregnation treatment, 6-mm-thick Japanese linden boards were impregnated with fire retardant, then three of them were laminated and planed to a total thickness of 15 mm. The total heat release for 10 min of the Japanese linden with $150\,kg/m^3$ of fire retardant and ceramic coating was less than $8\,MJ/m^2$ and that with $230\,kg/m^3$ of fire retardant was less than $3\,MJ/m^2$. The ceramic coating was resistant to light and moisture. The CRB coating had better fire performance and weatherability than AR, OS, and UP.

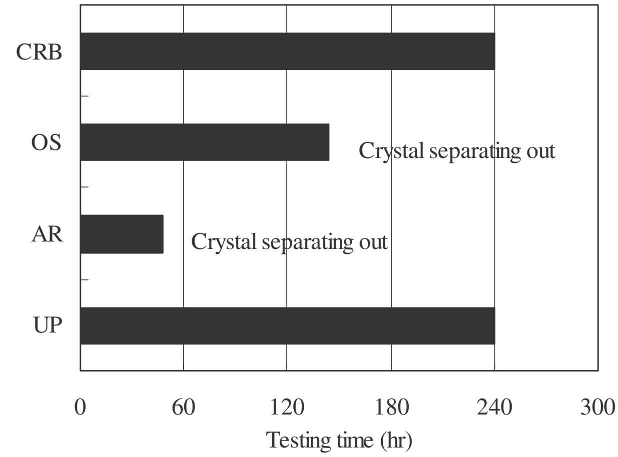

Fig. 8. Resistance to humidity of coated fire-retardant-treated Japanese linden board. The resistance to humidity was evaluated according to JIS K 5600-7-2 (continuous condensation) at 50°C and at 95% relative humidity. Samples treatments are as described in Fig. 7

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